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EVOLUTION AND CHEMICAL STATE OF OXYGEN UPON ACID DISSOLUTION OF $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$

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ABSTRACT. Gas chromatography/mass spectrometry was used to analyze the oxygen evolved from normal and ^{18}O enriched $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$ upon dissolution in normal and ^{18}O enriched acid. From the $^{18}\text{O}/^{16}\text{O}$ ratio we show that the oxide phase is the source of all the evolved oxygen. Our results indicate that some of the lattice oxygens are in a state other than O^{2-} , probably O^- or peroxide. The fact that we are unable to chemically detect peroxide suggests that the radical O^- could possibly be the species released from the oxide.

MATERIALS INDEX: Superconductors, perovskites, peroxides

Introduction

In order to formulate a mechanism(s) explaining high temperature superconductivity, experimental data in a number of areas are required. One of these is the nature of the holes which are generally recognized as being necessary for superconductivity to occur in these oxide materials (1-4). In fact, they are a common denominator in both the $\text{La}_2\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_y$ systems and likely play a similarly important role in the bismuth and thallium high T_c superconductors. We know that La_2CuO_4 as a stoichiometric compound is non-superconducting but becomes so by doping with divalent alkaline earths or by stoichiometry variations. In general, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ shows no superconductivity until sufficient holes are introduced by oxygen intercalation into the lattice. There is increasing evidence, both experimental and theoretical, that these holes are either on the oxygens, or in any case in the anion band rather than on the copper (5,6). If this were the case one could consider an unusual O^- type species and/or peroxide groups in the anion lattice rather than a O^{2-} and Cu^{3+} , and look at the dissolution reactions somewhat differently (7). For example, will a solid containing an O^- type species act like a peroxide upon dissolution in acid solution, or will it be indistinguishable from other materials where the hole is associated with the cation and the oxygens are thought to be mainly O^{2-} ions?

It was previously shown that the hole concentration can be determined directly by chemical means although it is not possible by this technique to determine the chemical identity of the particles carrying the holes (3,8). Another conclusion which one can draw from the chemical determination of holes is that whatever carries the holes is likely being transferred to the solution where it reacts with ions such as Fe^{2+} or I^- . However, the dissolution of those compositions containing holes, i.e. those with $y > 6.5$, in the absence of oxidizable species (Fe^{2+} or I^-) results in the evolution of oxygen. This also does not allow one to distinguish between Cu^{3+} and O^- since both will lead to oxygen evolution. One possible way to distinguish between them is by determining the source of the evolved oxygen - whether it is from the solution or the solid. It is well known that Cu-ions in aqueous solution are present as hydrated complexes, $\{\text{Cu}(\text{OH})_6\}^{2+}$, and that the water of this complex is rapidly exchanged with other water molecules from the solvent (9). This means that only a fraction of the oxygen atoms required for coordinating of the Cu^{2+} ions in solution can originate from the sample. On the other hand, Cu^{3+} hydrated complexes are unstable in solution and will evolve oxygen. Since our earlier work showed that, if present, they live long enough to carry the hole into the solution they are also likely to be hydrated before decomposition. Peroxides on the other hand do certainly not exchange oxygen atoms with the solvent because the bond in $(\text{O} - \text{O})^{2-}$ is much too strong. Thus, if the oxygen evolved were shown to originate from the solid, it is likely that it is due to the presence of a peroxide or a species such as O^- in the lattice. Therefore, a simple and direct experiment to determine the chemical nature of the hole-states is to do dissolution studies on ^{18}O enriched material. For example, if we dissolve a superconductor containing only ^{16}O in an ^{18}O solution, if Cu^{3+} is the hole carrier we would expect the evolved oxygen to contain up to about 20% ^{18}O , depending on the lifetime of the Cu^{3+} complex compared with the rate of the water-exchange between the complex and the solution. If, on the other hand, the holes are carried by oxygen, either in the form of a peroxide or O^- , we would expect a larger fraction of the evolved oxygen to be ^{16}O . Similarly, we can dissolve an ^{18}O enriched solid in a pure ^{16}O solution and thus, if the hole carriers are peroxide-like such as O^- , the evolved oxygen should be enriched in ^{18}O . These results will be presented, as well as those experiments designed to decide between O_2^{2-} and O^- as the probable "hole carrier" into the solution, plus additional information on ^{18}O intercalation in $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBC).

Experimental

The $\text{YBa}_2\text{Cu}_3\text{O}_y$ was prepared from the nitrates. The appropriate quantities of Cu metal (99.999%), assayed Y_2O_3 and BaCO_3 were dissolved in nitric acid, evaporated to dryness and converted to the oxide by heating in oxygen. After repeated heating and regrinding x-ray diffraction showed well crystallized single phase YBC. This oxygen content, y , of this material was then adjusted to 6.96 - 6.98, as determined by TGA and wet chemical analysis. It was then vacuum annealed at 550°C for 18 hours. The resulting material was a fine-grained tetragonal powder with $y = 6.1 - 6.2$, and was used as the source material in the subsequent experiments. The oxygen deficient powders were reoxygenated at various temperatures and times and then rapidly quenched. Two series of samples were prepared; one in pure ^{16}O : and the other in pure ^{18}O . The quenched samples were then analyzed for total oxygen, hole concentration and the $^{18}\text{O}/^{16}\text{O}$ ratio.

Total oxygen was determined in several ways: by the complete reduction to the metal using the TGA technique, and from analysis of the metallic species by inductively coupled plasma atomic emission spectrometry, and determining the oxygen by difference. We also obtained the oxygen concentration from a determination of the average oxidation state of the copper. This is also a direct measure of the hole concentration, p , which in fact is just the electron deficiency.

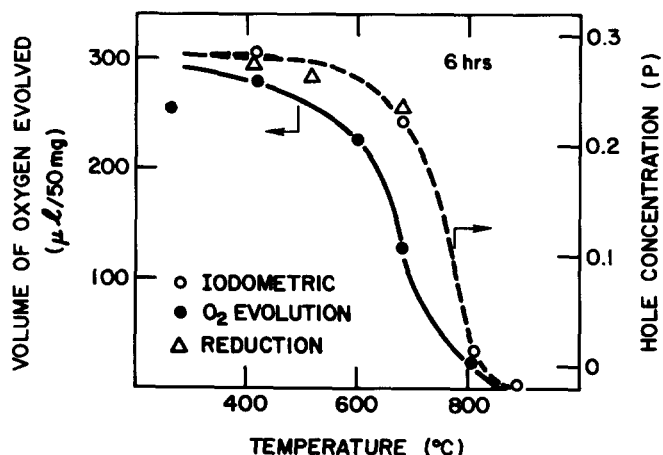
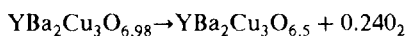


Fig. 1

Comparison of the hole concentration, P , as determined by Iodometric Titration (broken line) with the volume of evolved oxygen (solid line) for samples quenched from various temperatures. The open triangles show P determined by hydrogen reduction.

Two methods were used to determine the hole concentration, p ; First was by the now well-established iodometric titration method where the degree of oxidation of copper beyond Cu^+ is determined (10). From this we obtain the hole concentration, p , and the "average copper valence" ($2 + P$), from which we obtain the oxygen content. Similarly, the hole concentration can be obtained by measuring the volume of oxygen evolved when these "hole-containing" materials are dissolved in acid solution.

For example, if we consider the reaction:



The average charge on the Cu is reduced from 2.32 to 2.00. This reduction can also take place thermally, e.g. in a TGA experiment, or by acid dissolution where the hole species is allowed to react with the solution to evolve oxygen rather than with I^- or Fe^{2+} . The quantity evolved will be a measure of the hole concentration, from which the oxygen stoichiometry can be determined. Further, analysis of the evolved gas by mass spectrometry allows us to determine its origin, e.g. what fraction comes from the solid as opposed to the solution in which it is dissolved. The evolved gasses were analyzed by gas chromatography/mass spectrometry (GC/MS). For these analyses, isotopically enriched or standard YBC (50-100 mg) were placed into a sealed reaction vial along with 5 ml of 10% ^{18}O enriched H_2O . The enriched H_2O was purified by distillation just prior to use and purged with oxygen-free nitrogen for 10 min to remove dissolved oxygen. Acid was introduced by injecting 250-500 μL of a 1:1 HCL solution. The evolved gas was analyzed with an HP 5970 GC/MS using a carbosieve S-II column. In our spectra the O_2 was fully resolved from the N_2 peak. The $^{18}\text{O}/^{16}\text{O}$ ratios of the evolved gasses were determined by measuring the peak intensities in the oxygen dimer region of the mass spectrum ($M/E = 32$ TO 36). Secondary ion mass spectrometry (SIMS) was used to determine the $^{18}\text{O}/^{16}\text{O}$ ratio in pellets pressed from the enriched powders. A Cameca 4f ion microscope was employed for this determination. The samples were bombarded with a beam of $^{133}\text{Cs}^+$ primary ions at 14.5 KeV and negative secondary ions were monitored. The evaluation of the secondary ion spectrum in the range $m/e = 15$ to 20 and high mass resolution were employed to evaluate potential mass interferences at $m/e = 16$ and 18. Since no significant mass interferences were observed, the ratio of $^{18}\text{O}/^{16}\text{O}$ secondary ions was measured with a faraday cup

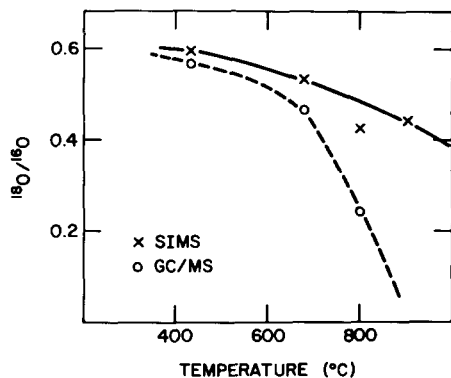


Fig. 2

The $^{18}\text{O}/^{16}\text{O}$ ratio for samples heated in pure ^{18}O gas and quenched from temperatures indicated. Solid line, as determined by SIMS, and broken line by gas chromatography/mass spectrometry.

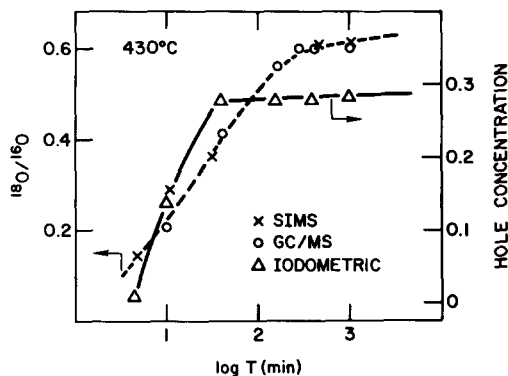


Fig. 3

The $^{18}\text{O}/^{16}\text{O}$ ratio (broken line) determined by SIMS (x) and GC/MS (O) and the hole concentration P (solid line), as determined by Iodometry, as a function of time at 430°C .

detector and a peak switching routine. In addition, samples were presputtered approximately 5 min (several thousand \AA) to remove anomalies caused by surface contamination.

To learn about the identity of the oxidizing species e.g. O_2^- , Cu^{3+} or O^- , released into the solution, 6-7 mg YBC samples were dissolved with grinding in phthalate-buffered solutions of $\{\text{MnEDTA}\}^{2-}$ in the presence of excess MnCl_2 , at $\text{pH} \approx 3$. The solution was buffered to $\text{pH} \approx 4$ with acetate, filtered, and its visible spectrum measured. The ratio between the resulting absorbances of the $\text{Cu}^{2+} - \text{EDTA}$ and $\text{Mn}^{3+} - \text{EDTA}$ complexes was compared with that obtained under similar conditions using $\text{Cu}(\text{NO}_3)_2$ and KMnO_4 standard solutions (the latter generates Mn^{3+} as follows: $\text{MnO}_4^- + 5\{\text{MnEDTA}\}^{2-} + 8\text{H}^+ \rightarrow 5\{\text{MnEDTA}\}^- + \text{Mn}^{2+} + 4\text{H}_2\text{O}$). A detailed account of this analytical procedure will be published separately (11). Since Mn^{3+} reacts with H_2O_2 "paradoxically", undergoing reduction to Mn^{2+} , one expects to see no Mn^{3+} if more than 50% (equiv.) of the oxidant is released as O_2^- ; on the other hand, if it is released as O^- (or Cu^{3+}) then the hole concentration found by this method should match the TGA and iodometric results.

Results and Discussion

In Fig. 1 we compare the hole concentration, p , expressed in terms of holes per copper site, as determined by iodometric titration, with that determined from measuring the volume of evolved oxygen. These measurements were made on samples heated in oxygen at the temperatures indicated, and then rapidly quenched. There is general agreement between the two techniques although the iodometric method gives a slightly higher value for p . The fact that both techniques show p going to zero (indicating no holes) in samples quenched from 900°C rather than the generally accepted temperature of around 720°C , in 1 atm O_2 , is undoubtedly due to oxidation of the powder during quenching. Because of the kinetics of the oxygen uptake, the sample quenched from 300°C was not fully oxygenated, hence the low volume of oxygen

evolved. The open triangles show the values obtained by complete reduction. In any case, as seen in Fig. 1, measuring the volume of oxygen evolved during dissolution is a reasonably accurate way to determine the hole concentration and oxygen content of these materials. Figs. 2 and 3 show the results of the ^{18}O incorporation in $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$. In Fig. 2, the $^{18}\text{O}/^{16}\text{O}$ ratio as a function of temperature, as determined by both SIMS and GC/MS, is shown. These samples were held at the indicated temperature for six hours in one atm ^{18}O and then rapidly quenched. The agreement between the SIMS and GC/MS is good for samples treated below 700°C . SIMS measures the bulk composition and since it agrees with the GC/MS indicates the data are representative of the materials bulk properties rather than some inhomogeneous surface process during the dissolution process. The samples used in the dissolution studies had an $^{18}\text{O}/^{16}\text{O}$ of about 0.58, meaning that about 37% of the lattice oxygen is ^{18}O . It is possible, however, by repeated vacuum deoxygenation and ^{18}O intercalation to produce samples with ^{18}O concentrations in excess of 75%.

Information on the rate of ^{18}O incorporation in $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$ is given in Fig. 3, where the $^{18}\text{O}/^{16}\text{O}$ ratio vs. time at 430°C is plotted. Clearly, for this temperature, the SIMS and GC/MS determinations are in good agreement and after about six hours, the material is fully oxygenated to $y = 6.96$. Also shown is the hole concentration, as determined by iodometry. It is a measure of the oxygen content and shows how it varies as a function of the reaction with oxygen under these conditions. These data are in general agreement with previous kinetic studies on oxygen uptake and emphasize the fact that there is an oxygen deficiency for the shorter reaction times (12).

Three experiments were done with the samples described above and the results are described in Table I. The first (run #1) was the dissolution of $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$ containing only ^{16}O in a solution containing only ^{16}O . The second (run #2) was the dissolution of the same YBC in an ^{18}O enriched solution; the third was the dissolution of 37% ^{18}O enriched YBC in acid containing only ^{16}O . In all cases the evolved oxygen was collected and the $^{18}\text{O}/^{16}\text{O}$ ratio determined as described above.

Table I

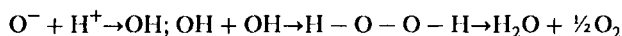
<u>RUN #</u>	<u>SOLID</u>	<u>SOLVENT</u>	<u>EVOLVED GAS</u>
1	YBC(16)	$\text{H}_2\text{O}(16)$	0.0030*
2	YBC(16)	$\text{H}_2\text{O}(18)$	0.0038
3	YBC(18)	$\text{H}_2\text{O}(16)$	0.43

* natural abundance $^{18}\text{O}/^{16}\text{O}$ the numbers in the parentheses, e.g.(18), indicate isotope enriched (^{18}O) or normal (^{16}O) ybc and solvent.

It is clearly seen from run 2, that the evolved oxygen contains no ^{18}O . Since its composition is identical to that of run 1, where the YBC was dissolved in a non-enriched HCL solution. In fact, in both cases the volume evolved corresponded to an oxygen content of $y = 6.96$. We can conclude from this that the "holes" in the solid YBC, whether they are Cu^{3+} , O^- or O_2^- , are not reacting with the solvent to form gaseous O_2 . If we now look at the results of run 3, where the ^{18}O YBC, containing the identical oxygen content, $y = 6.98$, is similarly dissolved in a non-enriched acid solution, we see the evolved oxygen is highly enriched in ^{18}O by a factor of about

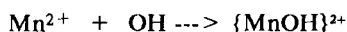
110, (compare runs 2 and 3). This shows unequivocally that when YBC containing holes is dissolved in acid solution and oxygen is evolved, its origin is from the solid and not the solvent. We recently became aware of a preprint of work by Salvador *et al*, where they report similar results on the dissolution of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-x}$ (13).

The question now becomes, what species in the solid and/or what dissolution mechanisms are responsible for the formation of the O_2 molecule which is evolved. The evolution of oxygen originating from the metal oxide rather than the solution, is extremely rare for compound metal oxides in contact with aqueous solutions, which implies that in these materials the oxygens are in a different state than O^{2-} ions. The two most likely species are the peroxide, O_2^{2-} , and O^- . Peroxide, as an entity itself in the solid, has been proposed on theoretical grounds (4,14) and indirectly "determined" experimentally (15). In addition, there is much spectroscopic data indicating strong covalently bonded O-O pairs consistent with peroxide bonds (5,7,16,17). However, because of their dynamic nature, structural studies have not been able to unequivocally identify the characteristic peroxide bond as one sees in BaO_2 , Na_2O_2 , etc. The O^- species can be thought of as a hole in the oxygen band as result of oxygen intercalation. To our knowledge there are no solids, other than peroxides, where the occurrence of an O^- entity has been unequivocally identified. Further, the magnetic moment expected from an O^- has not been seen experimentally. On the other hand, there is some theoretical evidence for its existence and spectroscopy studies, referenced above, show what appears to be a characteristic O^- signature. The formation of an oxygen molecule by the pairing of two O^- holes is likely since O^- has a $2p^5$ (fluorine) configuration and an unsaturated bond available to form an oxygen molecule according to the reaction:



(the latter step is catalyzed by Cu^{2+}). Similarly, one can argue that if the hole were on the copper i.e. Cu^{3+} , and the lattice oxygens are O^{2-} , the formation of an O_2 molecule is energetically unlikely. This is because O^{2-} ions have a $2p^6$ (neon) configuration with a valence of zero, hence have no tendency, either theoretically or experimentally, to form a covalent bond resulting in O_2 formation. Also if Cu^{3+} were present, one would expect that at the oxide/solution interface it would oxidize water forming O_2 , which is not seen experimentally.

A final point as to the identity of the oxidizing oxygen species released into the solution. Since we show that Cu^{3+} is highly unlikely, the question is; can we distinguish between O_2^{2-} and O^- ? We find that oxidation of $\{\text{MnEDTA}\}^{2-}$ by dissolving YBC is nearly quantitative. Based on comparison with TGA results, and assuming that the small discrepancy is wholly due to the presence of H_2O_2 (which reduces some $\{\text{MnEDTA}\}^-$ back to $\{\text{MnEDTA}\}^{2-}$), we can put an upper limit of 2% on the amount of oxidant released as O_2^{2-} . This closely matches the results of Harris and Vanderah (18) who used the related reaction of KMnO_4 with YBC. Further, upon the addition of a Ti^{3+} reagent, we were unable to observe the orange-yellow color of peroxytitanic acid which should form if H_2O_2 were present. We should point out that these tests are mainly used for ionic type peroxides (alkali and alkaline earths) and may not be entirely valid for the more covalent transition metals. The species released into solution is thus likely to be the anion radical O^- , which is instantaneously protonated to OH and, in the absence of oxidizable species, will quickly form gaseous oxygen. The H_2O_2 species, we show in the above reaction, does not appear to react with the Ti^{3+} reagent to yield the yellow peroxytitanic acid, probably as a result of its rapid decomposition catalyzed by Cu^{2+} at the solid/liquid interface. When large concentrations of the oxidizable species are present, the hydroxyl radical will react with them before having a chance to find another of its kind, e.g.



We note that the reaction of OH radicals with $\{\text{MnEDTA}\}^{2-}$ has been observed to proceed through attack on the ligand and to yield no Mn^{3+} (19). We believe our case to be different, due mainly to the use of much larger reagent concentrations and a large excess of MnCl_2 . Nevertheless, this fact as well as the need for additional data prevent one from completely ruling out other peroxide-type species (in particular copper-peroxide complexes or superoxide (O_2^-))(20) which may be stable enough to react with Mn^{2+} faster than they form H_2O_2 .

In conclusion, we show that the oxygen evolved by the acid dissolution of hole-containing superconducting oxides comes from the solid and not the solution, which is evidence that the holes are likely located in the oxygen band and not on the Cu as Cu^{3+} . It also implies that some of the lattice oxygens are not in the "normal" O^{2-} state but rather have a configuration consistent with O^- or peroxide, O_2^{2-} . Since we were unable to detect peroxide by chemical means, we speculate that the species released into the solution is the anion radical O_2^- ; however, additional work is required to verify this and to show it exists in the solid as a entity distinct from peroxide.

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References

1. P. W. Anderson, *Science*, **1196** (1987).
2. V. J. Emery, *Phys. Lett.* **67**, 2794 (1987).
3. M. W. Shafer, T. Penney and B. Olson, *Phys. Rev. B* **36**, 4047 (1987).
4. R. A. de Groot, H. Gutfreund and M. Weger, *Solid State Comm.* **63**, 141 (1987).
5. T. Kachel, P. Sen, B. Dauth and M. Campagna, *Z. Phys. B* **70**, 137 (1988).
6. F. J. Himpsel, G. V. Chandrashekhar, A. B. McLean and M. W. Shafer, *Phys. Rev. B*, (in press).
7. B. K. Chakraverty, D. O. Sarma and C. N. R. Rao, *Physica C* **156**, 413 (1988).
8. M. W. Shafer, R. A. de Groot, M. M. Plechaty and G. J. Scilla, *Physica C* **153-155**, 836, (1988).
9. J. E. Wertz, *J. Am. Chem. Phys.* **24**, 484 (1956).
10. A. I. Nazzari, Y. V. Lee, E. M. Engler, R. O. Jacowitz, Y. Tokura and J. B. Torrance, *Physica C* **153-155**, 1367 (1988).
11. E. I. Cooper (to be published).
12. I. Haller, M. W. Shafer, R. Figat and D. B. Goland, *Chemistry of Oxide Superconductors* - Edited by C. N. R. Rao, Blackwell Scientific Pub., 93 (1988).
13. P. Salvador, E. Fernandez-Sanchez, J. A. Garcia Dominguez, J. Amador, C. Cascales and I. Rasines, (preprint) submitted to *J.A.C.S.*
14. J. B. Goodenough, *Mat. Res. Bull.* **23**, 401 (1988).
15. A. Manthiram, X. X. Tung and J. B. Goodenough, *Phys. Rev. B* **37**, 3734 (1988).
16. D. O. Sarma and C. N. R. Rao, *Solid State Comm.* **65**, 47 (1988).
17. B. Dauth, T. Kachel, K. Fischer and M. Campagna, *Z. Phys. B* **68**, 407 (1988).
18. D. C. Harris and T. A. Vanderah, (submitted to *Inorg. Chem.*).
19. J. Lati and D. Meyerstein, *J. Chem. Soc. Dalton* **1105**, (1978).
20. J. E. Schirben, B. Morosin, R. M. Merrill, P. F. Hlava, E. L. Venturini, J. F. Kwak, P. J. Negrey, R. L. Baughman and D. S. Ginley, *Physica C* **152**, 121 (1988).